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SHIROTA TSUNEO**(54) FLUORESCENT LIGHT EMITTING MARKING METHOD****(57)Abstract:**

PROBLEM TO BE SOLVED: To form an image having high fluorescent light emitting intensity by printing the surface of a medium to be printed with aqueous fluorescent ink by an ink jet printer, and emitting exciting energy on the printing surface to emit the fluorescence.

SOLUTION: Aqueous fluorescent ink to be used contains fluorescent dye, transparent solid fine particles having particle size of 1 μm or less and water as solvent as indispensable ingredients, and as required various additives. The dye fluorescent emits by emitting various exciting energy, and is suitably selected according to the using purpose. The ink is discharged to the surface of a medium to be printed by an ink jet printer, and printed in a desired mode to form a mark. It is emitted with the exciting energy in addition to the marking, fluorescent emitted, and the mark is read. The type of the energy is suitably selected according to the type of the fluorescent dye mixed, and the energy of the type for satisfactorily absorbing by the dye is emitted. Thus, the mark having high fluorescent light emitting intensity can be formed.

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[Claim(s)]

[Claim 1] A firefly luminescence marking method characterized by printing on a printing hand-ed front face with an ink jet printer using aquosity fluorescence ink containing fluorescent dye and a transparence solid-state particle with a particle size of 1 micrometer or less, irradiating excitation energy and carrying out firefly luminescence on the printing front face.

[Claim 2] A firefly luminescence marking method according to claim 1 characterized by being the color in which fluorescent dye hardly absorbs excitation energy of wavelength which is 400-600nm, but absorbs excitation energy with a wavelength of 650-900nm, and emits fluorescence.

[Claim 3] A firefly luminescence marking method according to claim 1 or 2 characterized by irradiating excitation energy with a wavelength of 650-900nm, and carrying out firefly luminescence.

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] About the firefly luminescence marking method, in more detail, this invention forms the high mark of the fluorescence luminescence with an ink jet printer, and relates to the firefly luminescence marking method to which excitation energy is irradiated and carries out firefly luminescence.

[0002]

[Description of the Prior Art] The fluorescence ink for jet printing used for the method of printing on a printing hand-ed front face with an ink jet printer using the ink containing fluorescent dye, and forming the mark of printing which irradiates excitation energy, such as ultraviolet radiation and infrared light, and carries out firefly luminescence, a graphic form, a bar code, etc. on the printing front face, and such a method is indicated by official reports, such as JP,62-5079,B, JP,62-24024,B, and ***** No. 500590 [six to], and is well-known.

[0003]

[Problem(s) to be Solved by the Invention] however, about a method or fluorescence ink given in these official reports In using the base material front face which has the absorbency of paper, cloth, etc. as a printing hand-ed Since the fluorescent dye in ink permeated and diffused to the printing hand-ed depths with the solvent, when the concentration of the fluorescent dye in a printing hand-ed front face fell, and firefly luminescence reinforcement became inadequate, especially the printing hand-ed [absorbent] was colored by Japanese ink etc., there was a trouble that this inclination was remarkable. Moreover, it was economically [operationally or] difficult to make high concentration of the fluorescent dye in a printing hand-ed front face.

[0004] This invention solves the above troubles in the firefly luminescence marking method by the ink jet printer of the conventional technology, and aims at offering the firefly luminescence marking method which it is made for a lot of fluorescent dye to remain on a printing hand-ed front face, namely, can carry out an excitation energy exposure and can form an image with high firefly luminescence reinforcement.

[0005]

[Means for Solving the Problem] A result of having studied many things in order that this invention persons might solve the above-mentioned technical problem, When it prints on a printing hand-ed front face with an ink jet printer using aquosity fluorescence ink which made a transparence solid-state particle contain Since it fixes without this particle permeating the printing hand-ed depths on a printing hand-ed front face and fluorescent dye tends to adhere to a front face of these particles even if a printing hand-ed front face is a base material front face with the absorbency of paper, cloth, etc. Osmosis to the printing hand-ed depths of fluorescent dye decreased, and, as a result, fluorescent dye concentration of a printing hand-ed front face became high, therefore knowledge that a high mark of firefly luminescence reinforcement was formed of an exposure of excitation energy was acquired, and this invention was completed. That is, a firefly luminescence marking method of this invention is printed on a printing hand-ed front face with an ink jet printer using aquosity fluorescence ink containing fluorescent dye and a transparence solid-state particle with a particle size of 1 micrometer or less, and is characterized by irradiating excitation energy and carrying out firefly luminescence on the printing front face.

[0006] This invention is explained below at details. Aquosity fluorescence ink used in this invention can use water as a transparence solid-state particle and a solvent with a fluorescent dye and a particle size of 1 micrometer or less as an indispensable component, and can contain a hydrophilic organic solvent, water soluble resin, various additives, etc. if needed further. The above-mentioned fluorescent dye is fluorescent dye which carries out firefly luminescence by various excitation energy exposures, such as

ultraviolet radiation, infrared light, or the light, it can respond in activity eye and a selection activity can be suitably carried out.

[0007] As fluorescent dye, specifically C. I. Fluorescent Brightening Agent 14, 24, 30, 32, 52, 54, 69, 79, 84, 85, 86, 87, 90, 104, 112, 113, 114, 119, 121, 134, 135, 152, 166, 167, 168, 169, 191, 192, 201, 204, 214, 216, 217, 218, 223, 226, 229, 234, 236, 239, 240, 242, 257, 260, 271, 290, 310, 311, 312, 313, 314, 315; C.I. Basic Red 1, 1-1; C.I. Basic Violet 10 and 11:1; C. -- I. Basic Yellow 35, 40, and 95; C. -- I. Basic Blue 7; P-quota phenyl; P-terphenyl; 2, 5-diphenyloxazole; 2-(1-naphthyl)-5-phenyl OKIZAZORU; 2-phenyl-5-(4-biphenyl)- 1, 3, and 4-OKIZA diazole; 3-phenyl-7-(1, 2-2H-naphth thoria ZORIRU)-coumarin; 3, 7-screw (diethylamino) FENOKISAZONIUMU nitrate; 3, 7-screw (diethylamino) FENOKISAZONIUMU nitrate; DTTCI which is a laser color (CAS registration number 3071-70-3), HDITCI (CAS registration number 23178-67-8), IR-125 (CAS registration number 3599-32-4), IR-132 (CAS registration number 62669-62-9), IR-140 (CAS registration number 53655-17-7), H.I.D.C. Iodide, etc. are mentioned as a typical (CAS registration number 36536-22-8) thing.

[0008] About these fluorescent dye, when a point of the storage stability of fluorescence ink for ink jet printing is taken into consideration, what dissolves in water or is distributed to stability is desirable, but even if it is hydrophobic fluorescent dye, it is usable by making it stick to a transparence solid-state particle with sufficient moisture powder stability beforehand. In this invention, when asking for forged prevention and formation of a mark which is not conspicuous while not irradiating excitation energy especially, although it is hard to check by looking, under the light, it is desirable to use fluorescent dye which carries out firefly luminescence by the other excitation energy exposure.

[0009] Specifically excitation energy (light) with a wavelength of 400-600nm is hardly absorbed, it is hard to check by looking with the naked eye, and 650nm or more of excitation energy with a wavelength of 750-900nm (infrared light) is absorbed preferably, and especially the aforementioned laser color that carries out firefly luminescence is desirable. In addition, although fluorescent dye which carries out firefly luminescence with excitation energy with brief wavelength like ultraviolet radiation can also be used, it has a defect that background fluorescence of a base material will interfere in that case.

[0010] In this invention, the aforementioned transparence solid-state particle is blended in order to make high fluorescent dye concentration of a printing hand-ed front face and to make a high mark of firefly luminescence reinforcement form. Namely, although fluorescent dye permeates in the case of a printing hand-ed with absorbency and it is easy to diffuse it with a solvent at the depths of a printing hand-ed in it, if a

transparence solid-state particle is blended into fluorescence ink A particle which these particles remained without permeating the depths of a printing hand-ed on a front face, and remained on the printing hand-ed front face sticks to a front stirrup of jet printing of fluorescent dye at the time of jet printing. It controls that fluorescent dye permeates the printing hand-ed depths, fluorescent dye concentration of a printing hand-ed front face becomes high, therefore a high mark of firefly luminescence reinforcement is formed of an exposure of excitation energy.

[0011] In addition, in this invention, "transparence" about a transparence solid-state particle also includes what will be colored if light is penetrated in addition to transparence of perfect semantics, and a thing which has become muddy. However, what does not penetrate light is unsuitable to this invention in order to reduce firefly luminescence reinforcement, and in order to soil a printing hand-ed.

[0012] When it is required and a point which is 1 micrometer or less and it is made to be easy to remain on a front face of a printing hand-ed is also taken into consideration about particle size of a transparence solid-state particle so that nozzle **** of a jet printer may not arise, it is 0.01-0.5 micrometers preferably. As these transparence solid-state particles, by minerals system, in order that titanium oxide, an iron oxide, a calcium carbonate, a barium sulfate, a silica, an alumina, etc. may be mentioned as a typical thing and these minerals system particle may improve distributed stability if needed, what performed surface treatment may be used.

[0013] Moreover, hollow-like resin particle manufactured from an acrylic-styrene copolymer given in official reports, such as JP,63-254176,A, etc. by nature system of organic; A non-hollow-like resin particle of a publication water-dispersion [various] etc. is mentioned to official reports, such as JP,4-337305,A, JP,5-214194,A, JP,6-16895,A, JP,6-136164,A, JP,6-298879,A, JP,6-322221,A, JP,6-322215,A, JP,7-53913,A, and JP,7-53730,A, as a typical thing. As a water-dispersion Nylon [commercial item which made a good thing of dyeing property by fluorescent dye, for example, N-methoxymethyl-ized nylon, it not only to have water-dispersion [stable] in this invention, but graft-ize an acrylic acid (meta) or N-methylol acrylamide 20 to 40% of the weight, TOREJIN FS-350 and TOREJIN FS-500(all are imperial chemistry industrial company make)] are desirable.

[0014] A solvent of aquosity fluorescence ink used in this invention is water, it is distilled water or ion exchange water preferably, and it is also possible to use together a part of water miscibility organic solvents, such as methyl alcohol, ethyl alcohol, isopropyl alcohol, dioxane, an acetone, a methyl ethyl ketone, carbitol, and dimethyl sulfoxide, if needed further.

[0015] Aquosity fluorescence ink used in this invention contains a component explained

above as an indispensable component, and it is suitable about those blending ratio of coal that 0.005 - 2 % of the weight and a transparency solid-state particle are [3 - 35 % of the weight and a solvent] 50 % of the weight or more preferably two to 45% of the weight 0.001 to 10% of the weight for fluorescent dye.

[0016] In addition, aqueous fluorescence ink used in this invention Furthermore, if needed, so that a transparency solid-state particle may adhere to a printing hand-ed front face firmly So that a particle adhering to a nozzle of an ink jet printer can remove easily Moreover, polyacrylic acid, Polyacrylate, a styrene-maleic-acid copolymer, a styrene sulfonic-acid-maleic-acid copolymer, Polyester, hydroxyethyl cellulose, polyvinyl alcohol, Water soluble resin, such as a malto sill cyclodextrin and a polyethylene glycol, can be contained in 1 - 45% of the weight of an amount. Furthermore, a lithium nitrate, a nitrous-acid lithium, ammonium sulfite, ammonium formate, Additives, such as dispersants, such as electric conductivity regulators, such as ammonium acetate, lithium halide, and thiocyanic acid soda, and an amine denaturation silicone system dispersant, and antiseptics, can be contained in 0.1 - 5% of the weight of an amount.

[0017] Moreover, aqueous fluorescence ink used in this invention needs to have a property which was adapted for printing by ink jet printer. That is, as for fluorescence ink, it is desirable for viscosity to be the range whose about 0.8 to 1.2 surface tension about 50 to 3000 ohm-cm and specific gravity is about 20-60 dynes/cm for abbreviation 1-10mPa.sec (20 degrees C) and specific resistance.

[0018] Aqueous fluorescence ink used in this invention carries out mixed stirring of all the above-mentioned components at once, or carries out mixed stirring of fluorescent dye, a transparency solid-state particle, and some solvents beforehand, makes fluorescent dye stick to a particle, carries out mixed stirring of these and the remainder component, and can prepare them by filtering and refining with a filter which has about 1 / ten or less pore size of a diameter of a nozzle of an ink jet printer subsequently used.

[0019] A method which various well-known printers can be used [method] from the former as an ink jet printer used in this invention, for example, makes ink breathe out by electrification control system, ink on demand, and thermal head is held as a typical thing.

[0020] In a firefly luminescence marking method of this invention, a mark is formed by printing in a gestalt which is made to breathe out the aforementioned aqueous fluorescence ink with an ink jet printer on a printing hand-ed front face, and asks for it on it. Thus, by having turned marking up and irradiating excitation energy, firefly luminescence of the mark is carried out and it becomes possible to decipher a mark by devices, such as viewing or an optical detector. If what is necessary is just to choose suitably according to a class of blended fluorescent dye and blended fluorescent dye

irradiates excitation energy of a class absorbed well, firefly luminescence of the class of excitation energy will be carried out.

[0021] Especially in a firefly luminescence marking method of this invention, the aforementioned laser color which is fluorescent dye which hardly absorbs excitation energy with a wavelength of 400-600nm, but absorbs excitation energy with a wavelength of 650-900nm is blended into ink, excitation energy with a wavelength of 650-900nm is irradiated, and a firefly luminescence marking method which carries out firefly luminescence is desirable.

[0022]

[Example] This invention is explained at details based on an example and the example of a comparison below.

After mixing fluorescent dye, a transparency solid-state particle, water soluble resin, an additive, and a solvent to homogeneity by the blending ratio of coal (unit: weight section) shown in the <preparation of aqueous fluorescence ink> table 1, the depth filter with an effective diameter of 0.5 micrometers filtered and refined, and aqueous fluorescence ink (A) - (F) was prepared.

[0023]

[A table 1]

表 1

水性蛍光インク		A	B	C	D	E	F
蛍光染料	I R - 1 4 0	0.02	0.02				
	I R - 1 2 5			0.02	0.02		
	H. I. D. C. Iodide					0.02	0.02
透明固体 微 粒 子	アクリル樹脂系非中空樹脂粒子 (平均粒径 0.2 μ m)					20	
	N-メトキシメチル化ナイロンのアクリル酸グラフト体樹脂粒子の水分散液 (NV 20%、平均粒径0.05 μ m)	55					
	透明酸化鉄 (平均粒径0.05 μ m)			15			
水 溶 性 樹 脂	ヒドロキシエチルセルロース						15
	ポリアクリル酸塩			4	15		
	ポリビニルアルコール		10				
溶 媒	イオン交換水	30	75	76	80	75	80
	エチルアルコール	5	5	5	5	5	5
	ジメチルスルホキシド	10	10				
アミン変性シリコン系分散剤				0.3		0.2	

[0024] Each front face of the postcard which smeared away the example 1 non-printed

postcard and, and the front face in India ink was made to breathe out aquosity fluorescence ink A with an electrification control-system ink jet printer, and dot printing was carried out. Although it was hardly able to check by looking under the light, when infrared light with a wavelength of 830nm was irradiated, firefly luminescence of each obtained dot printing was carried out.

[0025] Dot printing was carried out like the example 1 except having used aquosity fluorescence ink B instead of the aquosity fluorescence ink A used in the example of comparison 1 example 1. Although it was hardly able to check by looking under the light, when infrared light with a wavelength of 830nm was irradiated, firefly luminescence of each obtained dot printing was carried out. The firefly luminescence reinforcement when irradiating infrared light in an example 1 and the example 1 of a comparison was measured using the spectrophotofluorometer. The result is shown in a table 2. In addition, the numeric value in a table 2 is shown as a relative value at the time of setting firefly luminescence reinforcement in the non-printed postcard of the example 1 of a comparison to 100.

[0026]

表 2

	実施例 1	比較例 1
(1) 無印刷ハガキ	1 5 0	1 0 0
(2) 墨塗りハガキ	4 5	5
蛍光発光強度比=(2)/(1) (%)	3 0	5

[0027] Firefly luminescence reinforcement was 1.5 times higher by the non-printed postcard compared with the case of the example 1 of a comparison which does not contain a transparence solid-state particle in the case of an example 1, and was 9 times higher by the Japanese ink coating postcard, and, in the case of the example 1, its firefly luminescence intensity ratio to the non-printed postcard of a Japanese ink coating postcard was also as high as 30% to 5% in the case of the example 1 of a comparison so that clearly from the data of a table 2.

[0028] Each front face of the postcard which smeared away the example 2 non-printed postcard and, and the front face in India ink was made to breathe out aquosity fluorescence ink C with an electrification control-system ink jet printer, and dot printing was carried out. Although it was hardly able to check by looking under the light,

when infrared light with a wavelength of 800nm was irradiated, firefly luminescence of each obtained dot printing was carried out.

[0029] Dot printing was carried out like the example 2 except having used aquosity fluorescence ink D instead of the aquosity fluorescence ink C used in the example of comparison 2 example 2. Although it was hardly able to check by looking under the light, when infrared light with a wavelength of 800nm was irradiated, firefly luminescence of each obtained dot printing was carried out. The firefly luminescence reinforcement when irradiating infrared light in an example 2 and the example 2 of a comparison was measured using the spectrophotofluorometer. The result is shown in a table 3. In addition, the numeric value in a table 3 is shown as a relative value at the time of setting firefly luminescence reinforcement in the non-printed postcard of the example 2 of a comparison to 100.

[0030]

表 3

	実施例 2	比較例 2
(1) 無印刷ハガキ	1 4 0	1 0 0
(2) 墨塗りハガキ	2 0	5
蛍光発光強度比=(2)/(1) (%)	1 4	5

[0031] Firefly luminescence reinforcement was 1.4 times higher by the non-printed postcard compared with the case of the example 2 of a comparison which does not contain a transparence solid-state particle in the case of an example 2, and was 4 times higher by the Japanese ink coating postcard, and, in the case of the example 2, its firefly luminescence intensity ratio to the non-printed postcard of a Japanese ink coating postcard was also as high as 14% to 5% in the case of the example 2 of a comparison so that clearly from the data of a table 3.

[0032] Each front face of the postcard which smeared away the example 3 non-printed postcard and, and the front face in India ink was made to breathe out aquosity fluorescence ink E with an electrification control-system ink jet printer, and dot printing was carried out. Although it was hardly able to check by looking under the light, when infrared light with a wavelength of 680nm was irradiated, firefly luminescence of each obtained dot printing was carried out.

[0033] Dot printing was carried out like the example 3 except having used aquosity

fluorescence ink F instead of the aqueous fluorescence ink E used in the example of comparison 3 example 3. Although it was hardly able to check by looking under the light, when infrared light with a wavelength of 680nm was irradiated, firefly luminescence of each obtained dot printing was carried out. The firefly luminescence reinforcement when irradiating infrared light in an example 3 and the example 3 of a comparison was measured using the spectrophotofluorometer. The result is shown in a table 4. In addition, the numeric value in a table 4 is shown as a relative value at the time of setting firefly luminescence reinforcement in the non-printed postcard of the example 3 of a comparison to 100.

[0034]

表 4

	実施例 3	比較例 3
(1) 無印刷ハガキ	1 3 5	1 0 0
(2) 墨塗りハガキ	2 0	4
蛍光発光強度比=(2)/(1) (%)	1 5	4

[0035] Firefly luminescence reinforcement was 1.35 times higher by the non-printed postcard compared with the case of the example 3 of a comparison which does not contain a transference solid-state particle in the case of an example 3, and was 5 times higher by the Japanese ink coating postcard, and, in the case of the example 3, its firefly luminescence intensity ratio to the non-printed postcard of a Japanese ink coating postcard was also as high as 15% to 4% in the case of the example 3 of a comparison so that clearly from the data of a table 4.

[0036]

[Effect of the Invention] The high mark of firefly luminescence reinforcement can be formed by the firefly luminescence marking method of this invention.